On the Structure of Trioxane Copolymers with Some Glycidylethers

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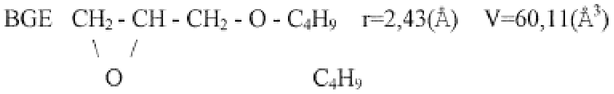
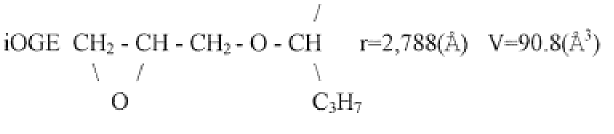
ABSTRACT: The changes of the polyoxymethylene (POM) structure by introducing comonomer units possessing side substituents (R) to the —O—CH_2—CH(R) units were studied. Various glycidyl ethers such as butyl (BGE), isooctyl (iOGE), and phenyl (PhGE) were used as comonomers with side groups of different size, volume, and steric hindrance. The influence of the quantity of the incorporated glycidyl ether (GE) comonomer units along the POM chain as well as both the type and size of the side substituent were investigated. The changes of crystallinity, melting temperature, heating and defect enthalpy, and the volume ($Å^3$) of the crystal lattice were calculated. Both the structure changes and thermal behavior were confirmed using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). Transmission electron microscopy (TEM), diffraction (TEMD) as well as scanning electron microscopy were used to investigate both structure and morphology. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2813–2823, 1999

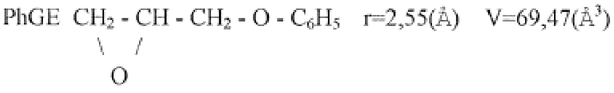
Key words: structure; morphology; comonomer; crystal lattice; lamellae

INTRODUCTION

Studies on the change of polyoxymethylene structure (POM) —$(OCH_2)_n$ by introducing units of —$O(CH_2)_n$—CH_2— with various values of n have been reported in the literature.[1–4] There is evidence about conformational changes occurring in trioxane (TO) phenylglycidylether (PhGE) copolymers containing up to 0.52 wt % of PhGE in the polyoxymethylene chain.[3] There are no more systematic investigations related to structural changes in copolymers possesing side substituents (R) to the O—CH_2—CH(R)— units. The study of TO copolymers with some glycidylethers, such as butyl (BGE), isooctyl (iOGE), and phenyl (PhGE), was of particular interest in this respect. With these copolymers, besides the changes in the main chain of POM by —$O(CH_2)_n$—O—CH_2— units, side substituents of different sizes were introduced as follows:


BGE $CH_2-CH-CH_2-O-C_4H_9$ r=2,43(Å) V=60,11($Å^3$)


iOGE $CH_2-CH-CH_2-O-CH(C_4H_9)(C_3H_7)$ r=2,788(Å) V=90.8($Å^3$)


PhGE $CH_2-CH-CH_2-O-C_6H_5$ r=2,55(Å) V=69,47($Å^3$)

It was also of interest to carry out copolymerization under conditions analogous to those in refs.

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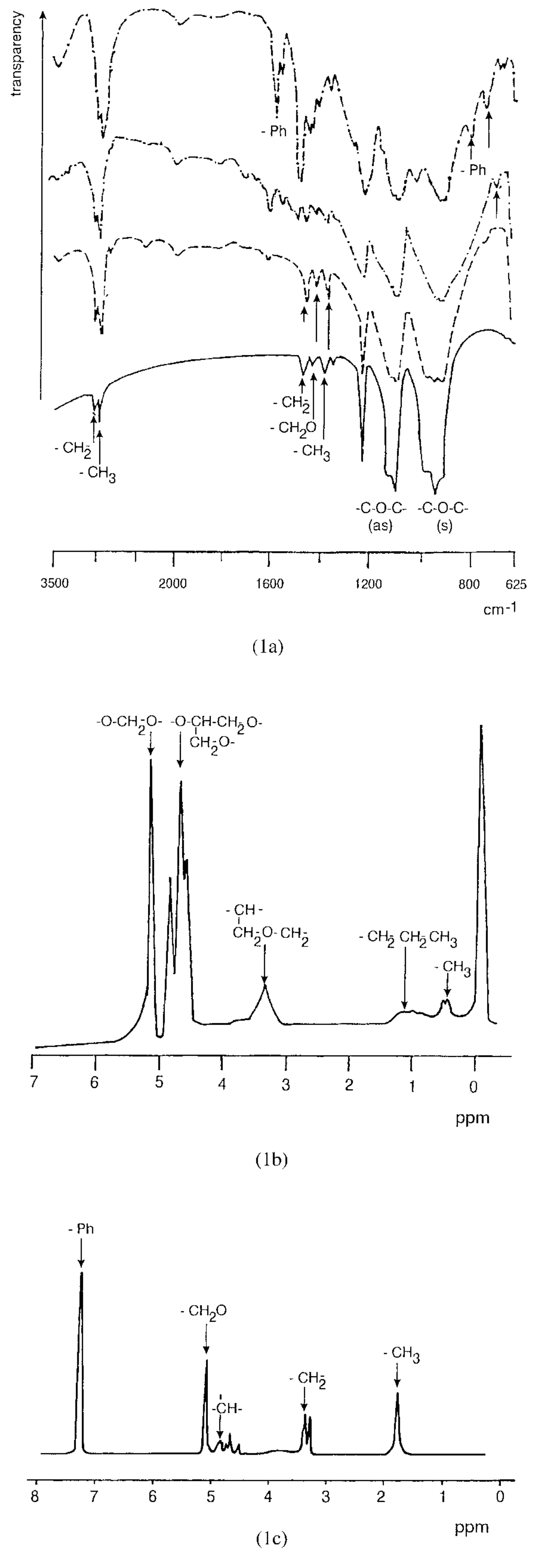


(1a)

(1b)

(1c)

Figure 1 (a) IR spectra of copolymers TO/GE: (b) ^{1}H-NMR spectra of TO/BGE; (c) TO/PhGE copolymers.

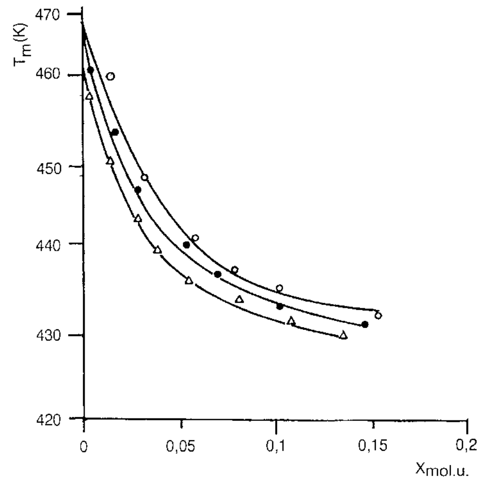


Figure 2 Melting temperatures (T_m) of TO/GE copolymers versus incorporated mol fraction of comonomer units: (○) BGE; (●) iOGE; (△) PhGE.

1–4, where polymer crystals with extended chain are obtained, and to consider the effect of the side units.

EXPERIMENTAL MATERIALS AND PURIFICATIONS

The trioxane (p.a.), a Fluka product, Switzerland, was purified according to ref. 5. The initiator BF_3OFt_2 (p.a.), (Fluka) was used after distillation BGE (p.a.) (Fluka) and was dried on CaH_2 follow-

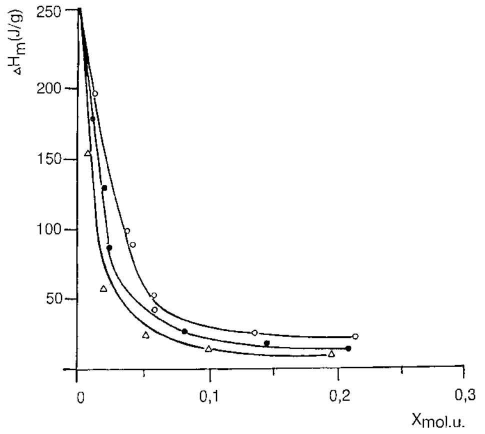


Figure 3 Heat of melting (ΔH_m) of TO/GE copolymers versus incorporated mol fraction of comonomer units: (○) BGE; (●) iOGE; (△) PhGE.

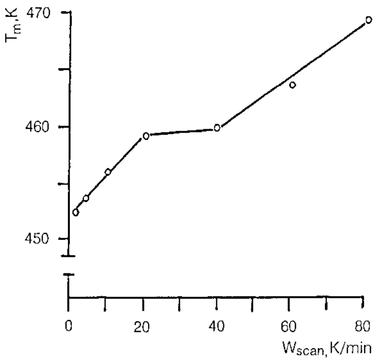
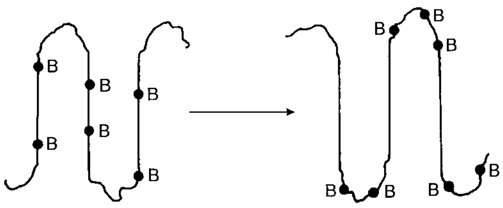


Figure 4 Melting temperaturs T_m of copolymers TO/PhGE (Xcom. = 9.1 mol %) versus scanning rate.

ing distillation in an argon atmosphere. PhGE (Fluka) (p.a.) was purified in an analogous way to BGE. iOGE was obtained and purified according to ref. 6 and 7.

Polymerization Conditions

The copolymerization was carried out in a 30% solution of TO nitrobenzene under argon atmosphere. Nitrobenzene was dried by means of P_2O_5 and distilled on CaH_2 according to a well-known method.[6] The quantity of initiator was varied from 0.5 to $4 \cdot 10^{-3}$ g · mol/g · mol monomeric mixture, depending on the mol percentage of the glycidylether.



Scheme 1

The copolymerization was a heteregeneous process. The break polymerization process was realized by means of $N(Et)_3$ in a 10-fold excess compared to the catalyst. When the copolymerization was over, the system was filtrated. The copolymer was washed by benzene and methyl alcohol, and dried in a vacuum at 60°C.[6]

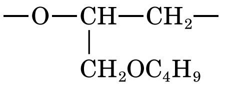
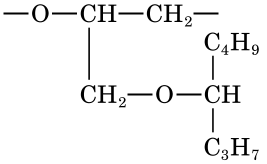
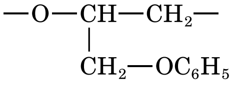
Analyses

The copolymer composition was conformed by elemental analyses on a Perkin-Elmer 240 apparatus in a KBr tablet.

The proton ^{1}H-NMR spectra were obtained on an INM-PS/JEOL, at 100 MHz using C_3OF_6 as a solvent and dimethylsulfooxide (DMSO) as the internal standard.

Both the TG and DSC investigation were recorded on a Perkin-Elmer thermograph, type TG-2 and DSC-2 at a heating rate of 20 K/min. The changes in the structure was followed by

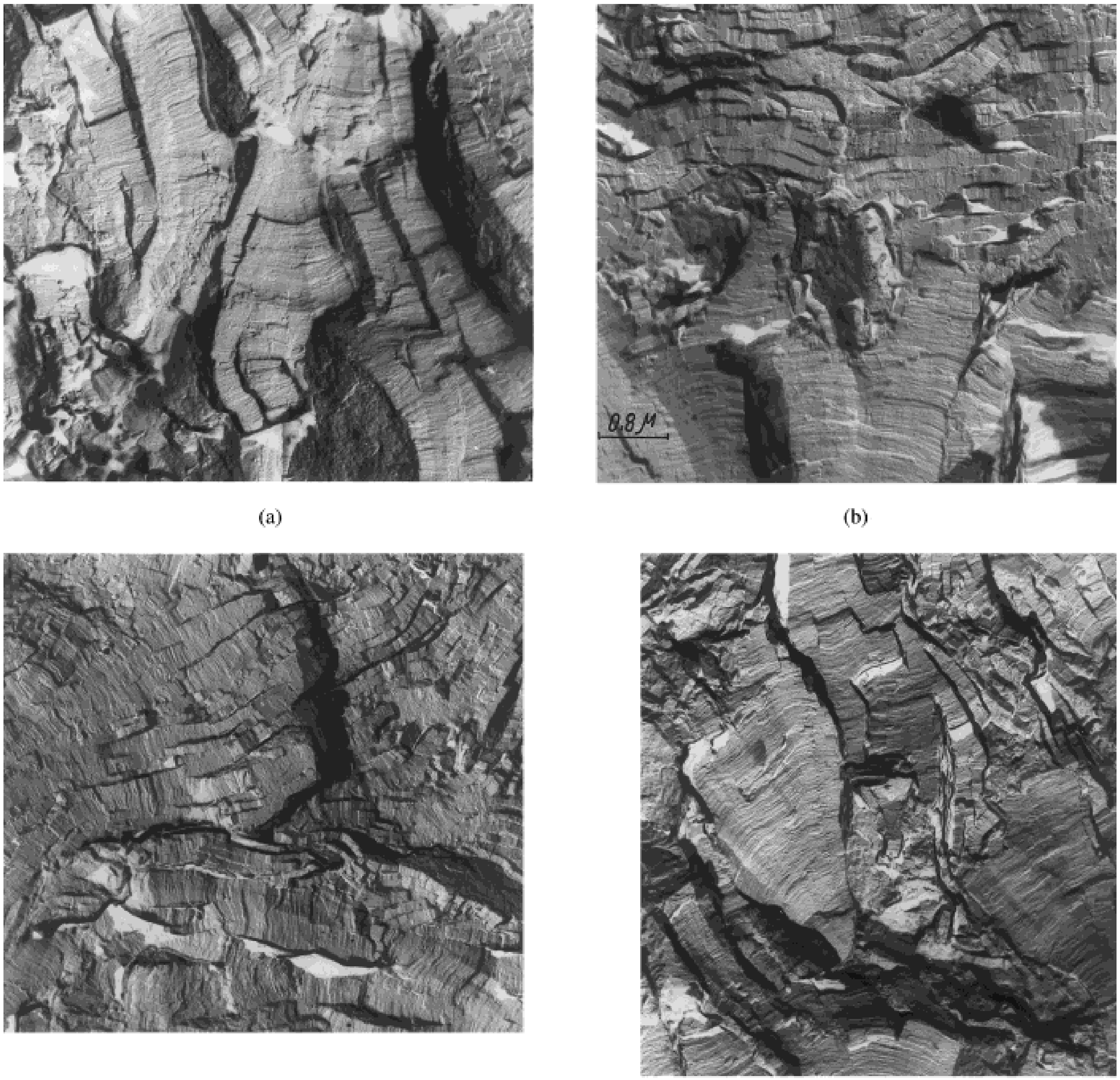
Table I Changes of H_D and T_D Values in Dependence of the Type of GE

Type of Comonomer Units	Units (Å)^3	$H_D \cdot 10^3$ (kJ/mol)	T_D (K)
1. BGE/TO	 $-O-\underset{\substack{\vert\\ CH_2OC_4H_9}}{CH}-CH_2-$ (60.11)	63.9	67.5
2. iOGE/TO	 $-O-\underset{\substack{\vert\\ CH_2-O-\overset{C_4H_9}{\underset{C_3H_7}{CH}}}}{CH}-CH_2-$ (90.8)	65.9	80.5
3. PhGE/TO	 $-O-\underset{\substack{\vert\\ CH_2-OC_6H_5}}{CH}-CH_2-$ (69.47)	67.23	82.37

means of a Philips X-ray diffractometer (30 kV, 30 mA) at a scanning speed of 1%/min (WAXS). The transmission microscope photographs (TEM) and transmission electron diffraction (TEMD) were obtained on a Philips-300; for TEMD, an accelerated voltage of 80 kV was used. The scanning electron microscopy (SEM) was performed on a JEOL apparatus.

RESULTS AND DISCUSSION

To follow the changes of the physical structure of TO copolymers with BGE, iOGE, and PhGE, copolymerization was carried out with the quantity of the incorporated glycidylether being varied within a vary large range from 5% to 50 mol %. The content of the copolymers of TO and GE were determined by NMR and IR spectra [Fig. 1(a–c)]. It is well known that the comonomer units in a copolymer chain could be distributed in the amorphous region of crystal lamellae or in both amorphous and crystal regions. In the first case, the temperature, enthalpy, and entropy of melting (ΔT_m, ΔH_m, ΔS_m) as well as the degree of crystallinity are not dependant on the quantity of incorporated comonomer GE units.$^{9-11}$ If the comonomer units are distributed statistically in the crys-

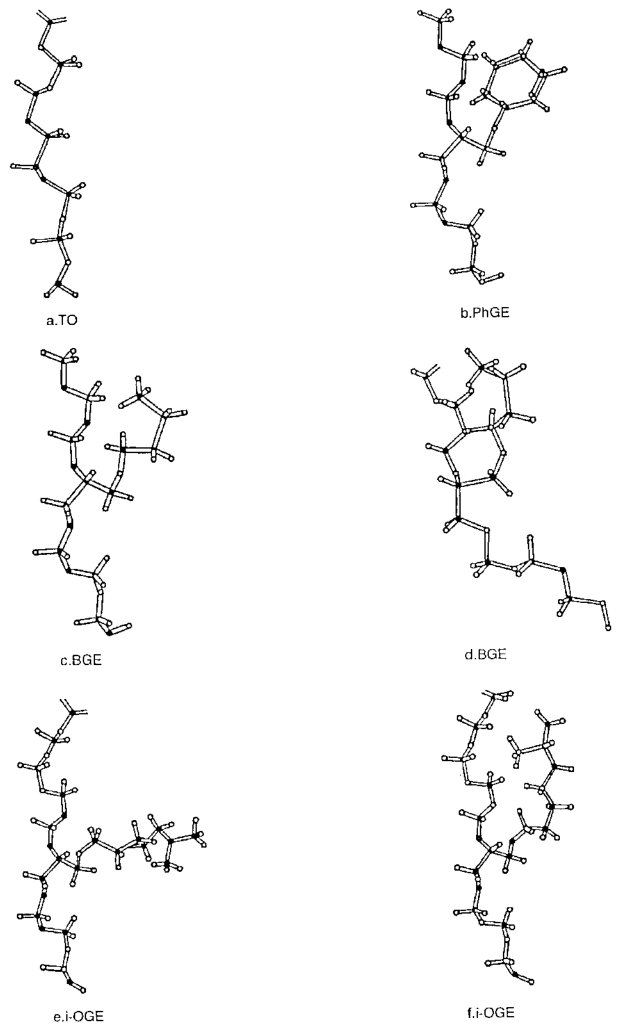


(a)

(b)

(c)

Figure 5 Election micrograph of a fracture surface of TO/GE copolymer crystals containing (a) TO/BGE (Xcom = 5.2 mol %); (b) TO/iOGE (Xcom = 6.1 mol %); (c) TO/PhGE (Xcom = 5.5 mol %).



Scheme 2

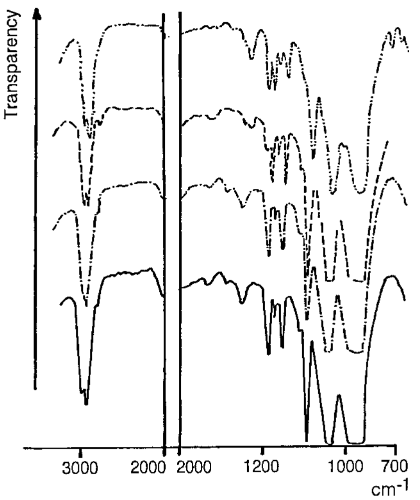


Figure 7 IR spectra of TO/GE copolymers at (—) BGE 5.2 mol %; (- • -) BGE 21.9 mol %; (— — —) PhGE 5.5 mol %; (- • • -) PhGE 19 mol %.

tal lamellae, then on increasing their concentration the defects of the crystal lattice will be increased.[12,13]

The DSC investigation on the thermal behavior of glycidylcopolymers (TO/GE) pointed out that there is a statistical distribution of the comonomer units along the polymer chain (Figs. 2 and 3). It is necessary to mention that it is very important to choose the appropriate heating rate by DSC invesigation so as to avoid recrystallization and superheating effects (Fig. 4). Below heating rates of 10–50 K/min, the recrystallization process and transition from extended into folded chain occurs.[14,15] Above the heating rate of 60–80

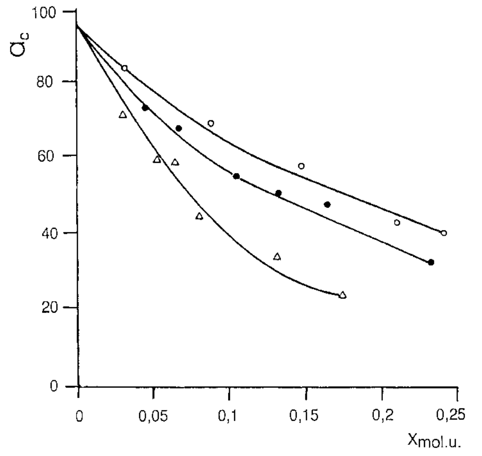


Figure 6 Dependence of degree of crystallinity α_{DSC} on the GE content: (○) BGE; (●) iOGE; (△) PhGE.

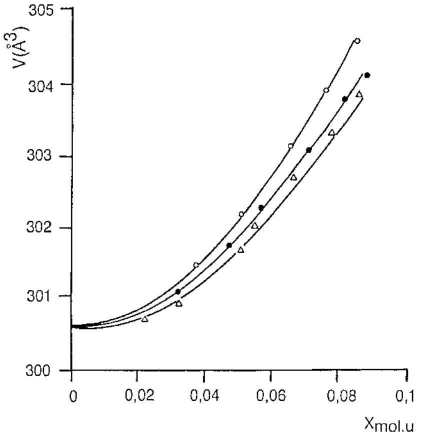


Figure 8 Changes in cell volume versus mol fraction of comonomer units of TO/GE copolymers: (○) BGE; (●) iOGE; (△) PhGE.

K/min thermal degradation and superheating effects could be observed.[14,16]

The investigations proved that the dependence T_m/Xcom and ΔH_m/Xcom have a complicated character (Xcom-mol fraction of incorporated comonomer units vs. TO units). At the limited degree of Xcom, depending on the nature of GE and polymerization conditions, T_m remains relatively constant despite the increasing of Xcom values (Fig. 4). This may be explained by the probable distribution of the most comonomer units in the amorphous regions in the lamellae (Scheme 1).

Also observed is a range where the T_m and ΔH_m values remained relatively constant, irrespective of increasing the Xcom content, most probably due to accumulation of comonomeric units at one point of the crystal lamellae, which act as bigger defects, as well as ejection of a significant part of the units to the amorphous region (Scheme 1). In the case of a statistical distribution of comonomer units in the crystal lamellae and as well as in the amorphous region, the following equation can be used:[12,13]

$$T_m = T^0_m[1 - H_D/\Delta H^0_m] \cdot \text{Xcom}$$

where T^0_m *and* T_m are the melting temperatures of homo- and copolymers, respectively; $H_D/\Delta H^0_m = \text{K}$ is calculated in the case, when the enthropy did not depend on the quantity of the incorporated comonomer;[16] H_D is the enthalpy of the melting of the defect regions, built by the incorporation of the comonomer in the crystal lattice; and $\Delta H_m{}^\circ$ is the melting enthalpy of the homopolymer.

From the slope of the curves (Figs. 2 and 3), the degree of defectiveness with different glycidyl comonomers could be obtained (Table I). As a result of the incorporation of BGE units along the copolymer chain insignificant changes in the values of H_m and T_m were found, i.e., the degree of defectiveness of the crystal structure. The melting temperature is with 5–18 K higher than that of the crystal obtained by recrystallization from the melt of the nascent crystals.

The crystal lamelle are thicker than 100–500 (Å) (Fig. 5). On the basis of all these results it could be concluded that the crystals are built from extended chains.[4] It is very interesting that monomer units of PhGE cause higher defects in the lattice in comparison to that of iOGE. The conformation of the side substituent (Scheme 2) may provide an explanation of this phenomena. The conformations shown in the Scheme 2 are possible because of the free rotation around the flexible —O—C— bond in the side substituent. The incorporated comonomer units in the crystal part of lamellae cause significant changes in the degree of crystallinity (α_c) and in the values of the crystal lattice parameters.[9–11]

The change of values α_c could be seen in Figure 6. α_c is calculated according to[17,18]

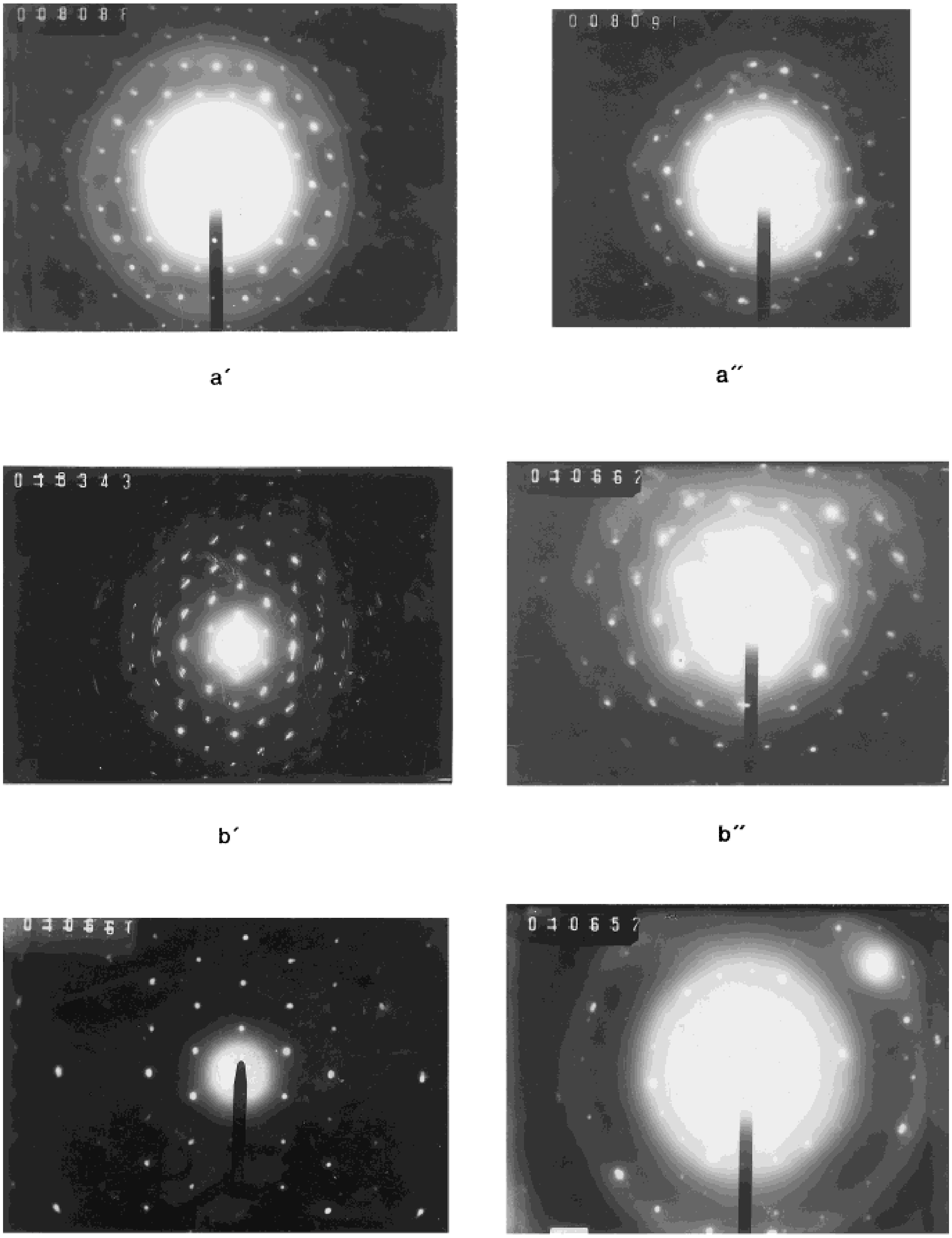
$$\alpha_c = \frac{\Delta H_e}{\Delta H_c}$$

where ΔH_e is the enthalpy of the experimental sample; ΔH_c is the enthalpy of 100 to crystal POM,[19a] and ΔH_c = 310 J/g.[19b]

The crystallinity was also defined from the maxima at 1235 cm^{-1} in the IR spectra (Fig. 7).[20] The experimental data show that the greater the steric hindrance of the side substituent in the comonomer units, the greater

Table II ***d*-Values of the Crystal Lattice of TO/GE Copolymers in Dependence of GE Content**

Type of GE	X_{GE} mol %	d_1 (Å)	d_2 (Å)	d_3 (Å)	d_4 (Å)	d_5 (Å)	d_6 (Å)	d_7 (Å)	d_8 (Å)	d_9 (Å)	d_{10} (Å)
	1.41	1.01	1.07	1.15	1.25	1.32	1.52	1.72	2.05	2.29	
BGE	6.52	1.08	1.11	1.20	1.27	2.10	2.19	2.29			
	21.83	1.09	1.32	1.63	1.76	2.25	2.63	2.76			
	2.70	0.97	1.01	1.05	1.11	1.17	1.19	1.32	2.05	2.29	2.63
iOGE	6.62	1.05	1.10	1.27	1.77	1.63	2.19	2.46	2.61	2.90	3.24
	16.71	1.05	1.22	1.36	1.85	2.37	2.76	2.82	2.90	3.05	4.02
	1.30	1.11	1.02	1.04	1.10	1.19	1.20	2.01	2.65	2.53	4.23
PhGE	7.33	1.02	1.19	1.22	1.49	1.58	2.31	2.53	3.81	4.23	4.48
	17.82	1.05	1.22	1.36	1.45	1.85	2.37	2.90	3.05	3.17	5.86



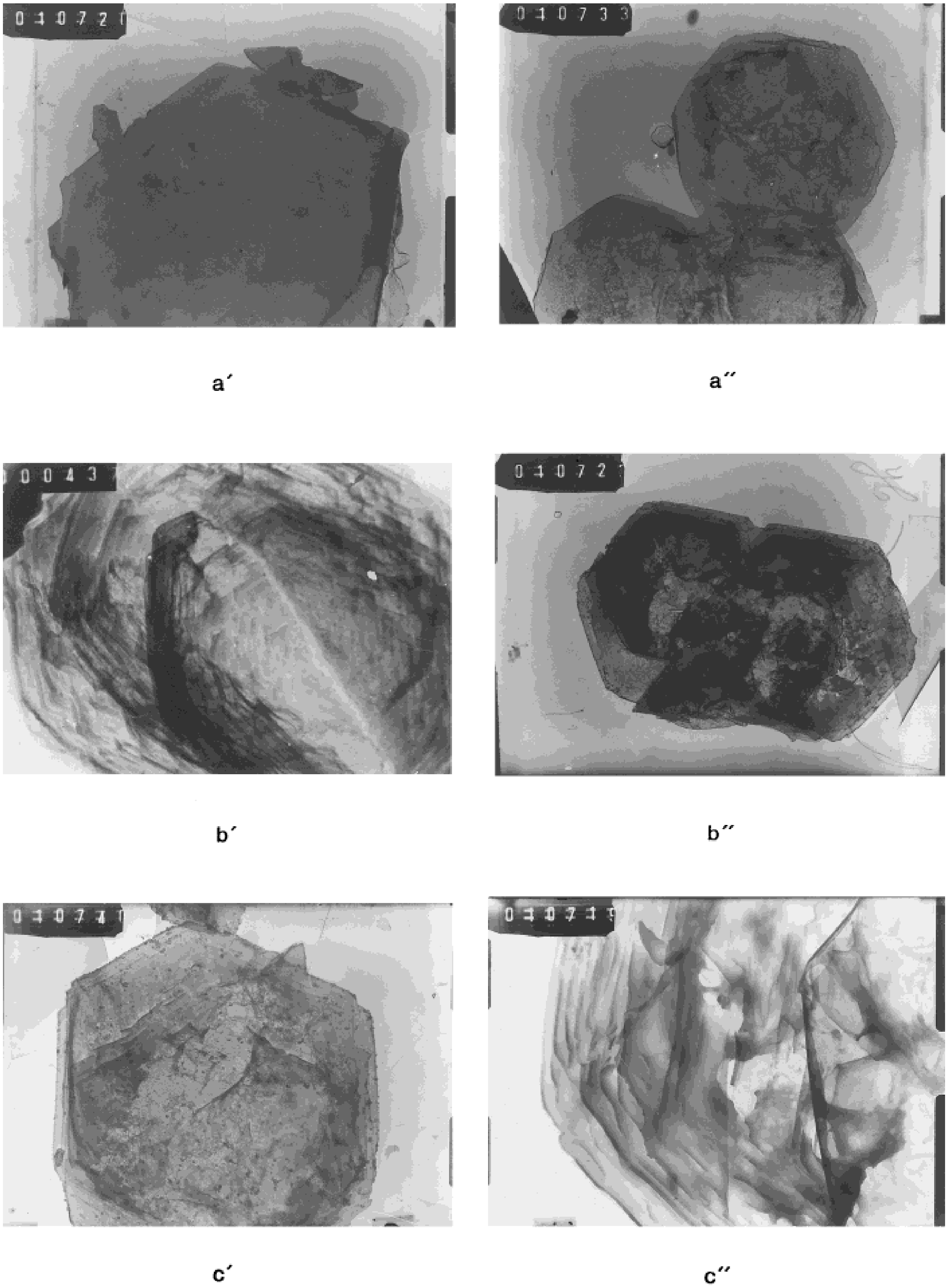
a′ a″

b′ b″

c′ c″

Figure 9 Electron microdiffractions of copolymers TO/GE at (a) TO/BGE; (b) TO/iOGE; (c) TO/PhGE. (a′) 1.2 mol % BEG; (b′) 1.6 mol % iOGE; (c′) 1.3 mol % PhGE. (a″) 9.2 mol % BEG; (b″) 9.5 mol % iOGE; (c″) 17.8 mol % PhGE.

the decreasing of the degree of crystallinity, respectively α_c, by the same content of GE Xcomon (Figs. 6 and 7). The disturbance in the lamellae structure lead to the significant alteration in the lattice parameter and in the volume, respectively (Fig. 8).



a′ a″

b′ b″

c′ c″

Figure 10 Election micrograph of TO/GE copolymers at (a) TO/BGE; (b) TO/iOGE; (c) TO/PhGE. (a′) 1.9 mol % BEG; (b′) 1.6 mol % iOGE; (c′) 3.8 mol % PhGE; (a″) 9.2 mol % BEG; (b″) 9.3 mol % iOGE; (c″) 9.8 mol % PhGE.

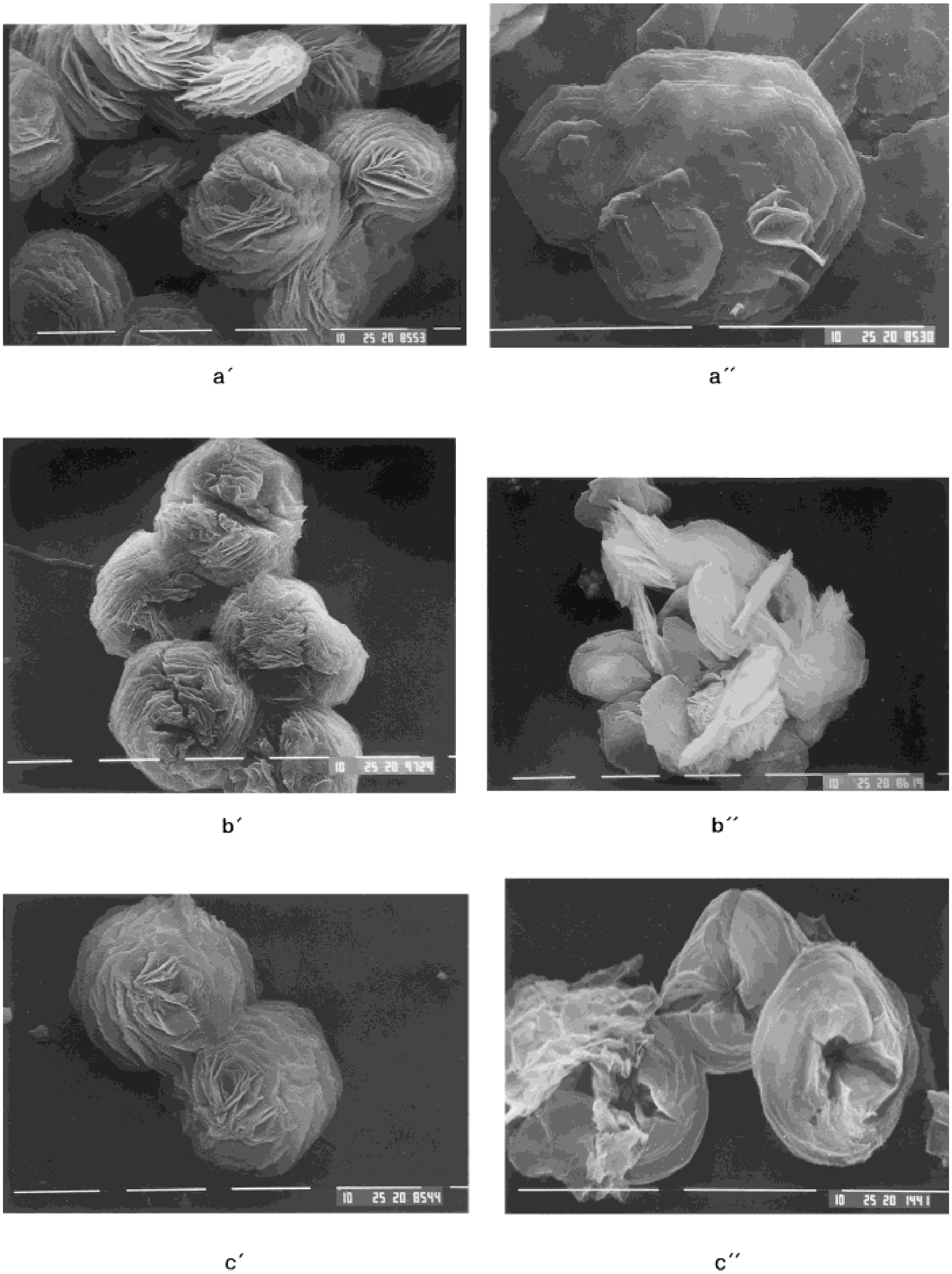


Figure 11 Scanning election micrographs (SEM) of TO/GE copolymers containing up to 20 mol % versus TO of GE: (a) TO/BGE; (b) TO/iOGE; (c) TO/PhGE. (a′) 1.2 mol % BEG; (b′) 1.6 mol % iOGE; (c′) 1.3 mol % PhGE; (a″) 9.2 mol % BEG; (b″) 9.5 mol % iOGE; (c″) 9.8 mol % PhGE.

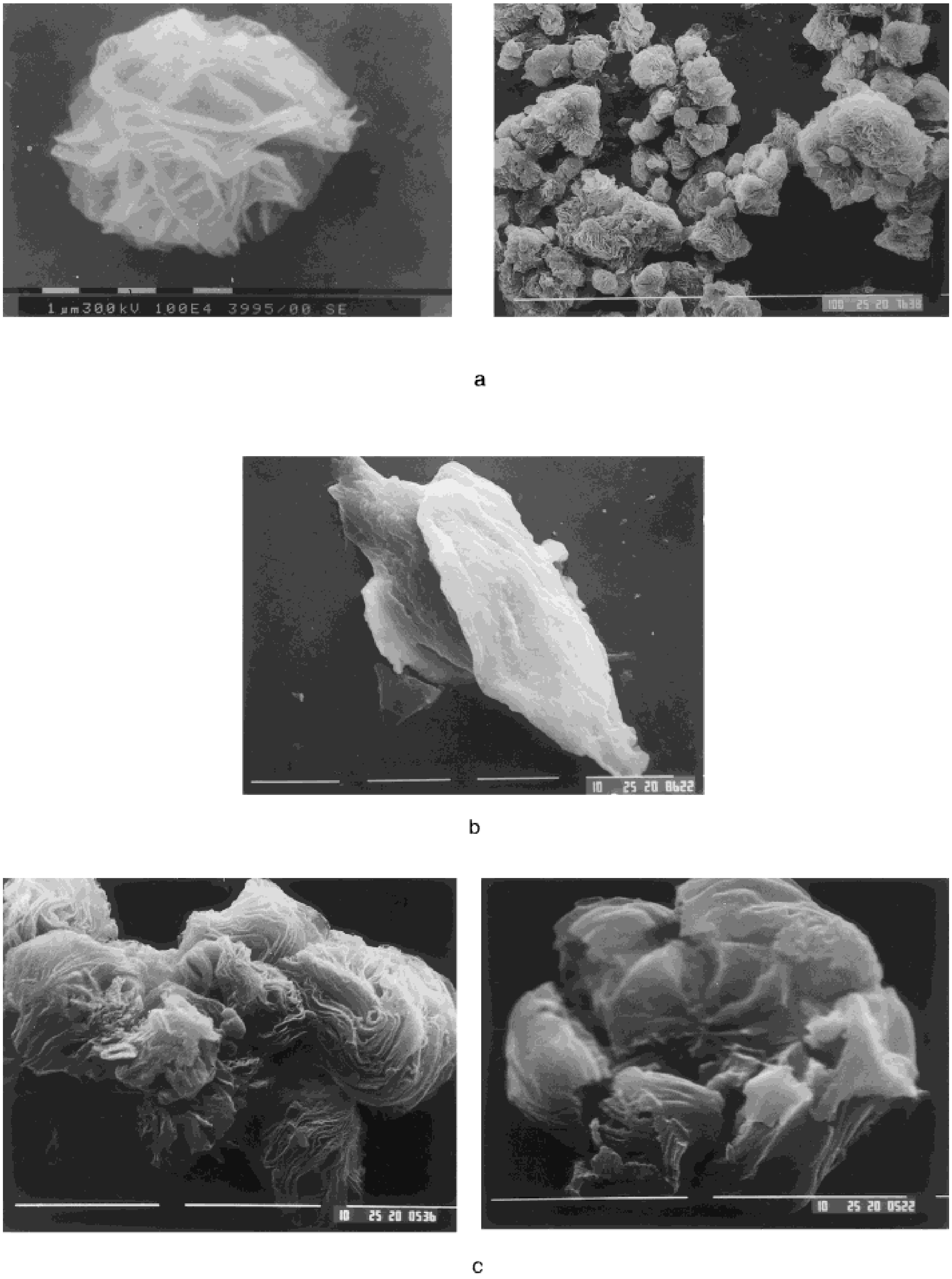


Figure 12 SEM of TO/GE containing more than 20 mol % of GE comonomer versus TO: (a) TO/BGE; (b) TO/iOGE; (c) TO/PhGE.

The TEMD data [Fig. 9(a–c)] demonstrated that the hexagonal structure—typical for POM crystals—remains, but significant changes in the d-parameters occur (Table II).

The electron microdiffraction pictures [Fig. 9(a–c)] of GE/TO monocrystals are clear evidence for the perpendicular position of folded chains to the lamellae surface.

In parallel with the changes in the crystal lattice, significant changes in the morphology of the crystals were observed [Fig. 10(a–c) TEM, Fig. 11(a)–(c) SEM, and Fig. 12(a–c)].

CONCLUSION

From all our investigations it may be concluded that the concentration of the comonomer units in the crystal part of the lamellae as well as the steric hindrance of the side substituent are of great importance for the structure of the copolymer GE/TO.

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